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PHOTOELECTRIC PROPERTIES OF INDIUM SULFIDE AND SELENIDE

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Figures referred to herein are appended. Numbers in parentheses refer to the bibliography at the end.

INTRODUCTION

The compounds of elements of the seventh series of Period V of Mendeleev's table with sulfur and selenium are sufficiently well known from the point of view of their photoelectric properties. The only exceptions are sulfides and selenides of indium. The position of indium in this series has permitted the assumption of the presence of an internal photoelectric effect in its compounds with sulfur and selenium.

The present work is devoted to the experimental study of this question.

There are only three well-known works on the compounds of indium with selenium and sulfur (1,2,3). They concern questions of the synthesis of these compounds and some of their chemical properties.

We investigated the photoelectric properties of the following compounds of indium: In_2S_3 ; InS ; In_2S_3 ; In_2Se_3 ; InSe ; and In_2Se_3 .

The material was prepared by fusion in a vacuum of selenium (or sulfur)

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and indium in corresponding weight ratios. The fused material was studied either in the form of filed and ground plates, or thin layers on glass, obtained by vaporization in a vacuum.

Photoconductivity was studied with the aid of intermittent light. The alternating potential difference developing in the specimen after amplification was registered by an electronic voltmeter.

The curves of distribution of the internal photoelectric effect on the spectrum were taken with the aid of a Leiss quartz monochromator.

It must be noted that the photoelectric properties were investigated both with and without the application of an electrical field. In the latter case the intermittent beam of light fell on the specimen asymmetrically in relation to the electrodes (closer to one of them). Alternating electromotive force also developed in the specimen. The character of photosensitivity was fundamentally the same in both cases.

PHOTOCONDUCTIVITY OF InSe and InS

Of all the compounds of indium and selenium studied by us, only InSe possessed great photoconductivity. Two other compounds, In_2Se and In_2Se_3 , possessed it to a very small degree.

Curve a in Figure 1 represents the spectral distribution of photoconductivity in a specimen of InSe prepared in the form of a ground plate. As may be seen, the maximum sensitivity lies in the near infrared zone of the spectrum.

The attempt to discover the photoconductivity of specimens obtained by vaporization in the form of layers on glass at first proved negative. It turned out to be necessary to heat the layers of InSe in a vacuum in order to obtain photoconductivity close to that of the original material in the character of spectral distribution.

Under certain conditions of temperature treatment of the layers it turned out to be possible to obtain the photoconductivity represented by b in Figure 1.

Preliminary experiments demonstrated that all compounds of indium with sulfur possess photoconductivity in a very small degree. Only the results obtained from the investigation of InS will be described below.

We failed to discover photoconductivity in plates of InS cut from a solid mass, because of the loud noises developing when voltages were applied to the specimen. The layers obtained by vaporization on glass also did not disclose photoconductivity. Initial heating in a vacuum, which brought about the development of photoconductivity in the case of layers of InSe, proved futile for InS.

It was thus established that the conductivity of InS obtained by vaporization and temperature treatment is significantly higher than that of the original material. This could occur on account of the dissociation of the compound during vaporization, with the development in the layers of an excess of metallic indium. Therefore, it seemed a natural idea to return the material to its original condition, subjecting it to the corresponding treatment in sulfur vapors.

A further stage in this plan was the investigation of the influence on photoconductivity of the treatment of layers of InS in sulfur vapors, and of InSe in selenium vapors.

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TREATMENT OF InSe LAYERS IN SELENIUM VAPORS

A glass plate with a deposited layer of indium selenide or sulfide was placed with a piece of selenium or sulfur in a glass ampoule, which, after evacuation (10^{-4} - 10^{-5} mm Hg) and unsoldering, was placed in an oven at a temperature of 200-300 degrees C.

The following results were obtained with indium selenide. Within broad limits of variation in temperature and time, the initial heating with selenium invariably led to an abrupt displacement of the curve of spectral sensitivity in the shortwave zone of the spectrum. Curve a in Figure 2 represent this new spectral distribution. As may be seen, the maximum is at 560 m μ instead of a maximum at 1,000 m μ inherent in the original material.

It may be noted that 10 minutes at a temperature of 200 degrees C (that is, with insignificant tensions of selenium vapors) is sufficient for a film of InSe with selenium to obtain a similar sensitivity.

Curve b in Figure 2 gives the distribution of sensitivity on the spectrum for pure selenium (the measurements were made with the same arrangement and under the same conditions).

The similarity of sensitivity on the spectrum between the layer of InSe treated with selenium and the character of the spectral sensitivity for pure selenium is striking.

In the treatment of layers of In₂Se₃ with selenium vapors (not photo-sensitive before treatment), photoconductivity also developed in them which, in the character of spectral distribution, can hardly be distinguished from the photoconductivity of layers of InSe treated with selenium vapors.

The presence of such concurrent spectral curves for pure selenium and layers of InSe treated with selenium might perhaps be explained in the following manner. In the treatment with selenium vapors a continuous selenium layer is formed on the surface of specimens. This layer also determines the photoconductivity observed. The layer of InSe has no part in the photoelectric effect. However, a number of experimental facts contradict this supposition.

Thus, for example, if selenium were to settle on the surface of the layer from above without penetrating the lattice of the substance, then the photoconductivity measured from the side opposite the selenium (through the glass and layer of InSe) should drop significantly and should change its spectral distribution. A test demonstrated that a change in the direction of the falling light does not influence the magnitude and spectral distribution of photoconductivity.

Later in the treatment with selenium vapors the layers of InSe changed from dark and opaque to red and semitransparent, which indicated the deep changes in the material.

In Figure 3 curves of absorption for the layer of InSe before and after treatment with selenium vapors are shown.

Finally, if selenium existed in the form of an independent continuous layer on the surface of the basic material, then the initial heating of the layers at $T = 300$ degrees C, with the purpose of eliminating the Se, would bring about the disappearance of photoconductivity in that zone of the spectrum. In fact, the spectral curves of photoconductivity taken before and after elimination cannot be distinguished from one another.

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Everything said above seems to indicate that introduction of selenium into the lattice of InSe had taken place here.

TREATMENT OF InS LAYERS IN SULFUR VAPORS

As already mentioned, InS does not show photoconductivity, in solid form or in layers obtained by vaporization. However, as a result of treatment in sulfur vapors, layers of InS acquire considerable photoconductivity.

Curve a in Figure 4 represents the spectral distribution of photoconductivity for layers of InS treated with sulfur. Here, there is a very interesting circumstance, namely, that the course of the curve and the position of the maximum are very little different from the spectral curve of photoconductivity for pure sulfur according to the data of Kurrelmeyer (4, 5) and Tartakovskiy and Rekalova (6). On Curve b in Figure 4, photoconductivity for sulfur has been adduced from the work of the latter authors for comparison. The maximum of photoconductivity for InS with an admixture of sulfur lies at 420 m μ . According to Kurrelmeyer, the maximum for sulfur is at 470 m μ ; according to the data of Tartakovskiy and Rekalova, at 480 m μ .

All considerations and experimental facts expounded in reference to the treatment of InSe in selenium vapors apply in an equal degree to layers of InS treated with sulfur vapors.

In addition to those described above, experiments were also made on the treatment of InSe in sulfur vapors and InS in selenium vapors.

In the first instance, the spectral distribution coincided with the distribution in InS after treatment with sulfur (Figure 4, curve a); in the second, with InSe after treatment with selenium (Figure 2 curve c).

DISCUSSION OF RESULTS

Photosensitivity in the infrared zone for InSe before its treatment in selenium vapors may be explained by the admixture of excess metallic indium. The disappearance of infrared sensitivity upon treatment in selenium vapors and the appearance of sensitivity in the visible zone of the spectrum is explained by the fact that upon treatment, the selenium takes up the excess indium. In addition, the infrared maximum disappears. Further introduction of an admixture of selenium brings about the appearance of a new "selenic" photosensitivity.

The very close correspondence between the spectral curves for selenium and InSe treated in selenium vapors, and likewise for sulfur and InS treated in sulfur vapors, makes one assume that photoconductivity in these cases has a purely admixtural character. The photoelectric centers are selenium and sulfur in atomic or low molecular condition, located in the structure of the substance in the form of a solid solution.

However, it is difficult to explain the indicated correspondence of spectral curves using the usual scheme. Actually, the role of the admixture in photoconductivity usually amounts to the creation of supplementary local levels in the barrier zone of the semiconductor. These levels may be either the levels of capture of the photoelectrons (penetration photoeffect), or the levels of emission of photoelectrons (electronic photoeffect).

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Not one of these possibilities can be accepted for an explanation of the correspondence of the spectral curves, because it is difficult to assume that local admixtural levels of selenium (or sulfur) must be distributed in the energy spectrum of InSe (or InS) in just such a way as to cause this correspondence.

It might be possible to accept a simpler explanation: The atoms of the admixture, entering the lattice of the basic substance, coagulate, forming inclusions of rather large dimensions. It is natural the photoconductivity in this case may have the same character as for the admixture in pure form.

However, this explanation is contradicted by the fact that the magnitude of photoconductivity in InS treated with sulfur is many times greater than the photoconductivity of pure sulfur.

In conclusion, the authors sincerely acknowledge their thanks to V. P. Zhuse for a number of valuable suggestions and for aid in the work.

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[Appended figures follow.]

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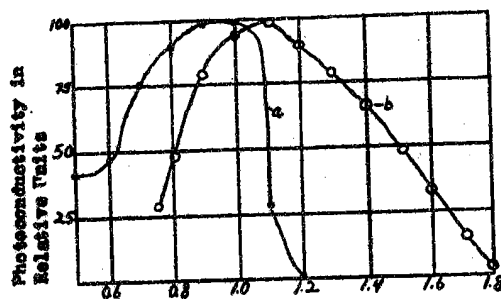


Figure 1. Spectral Sensitivity

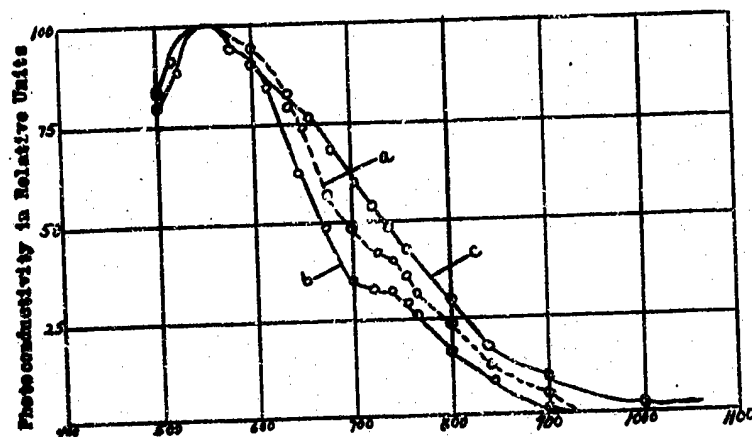


Figure 2. a - Photoconductivity of layers of InSe - Se;
 b - Photoconductivity of pure Se;
 c - Photoconductivity of layers of InS - Se.

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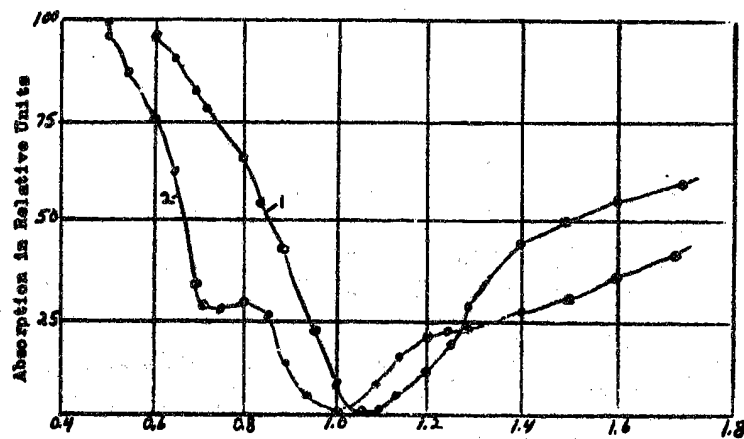


Figure 3. 1 - Absorption of light in layer of InSe before treatment with selenium; 2 - Absorption of light in layer of InSe after treatment with selenium.

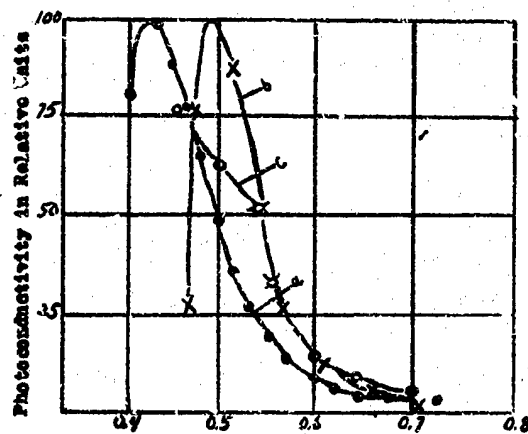


Figure 4. a - Photoconductivity of layers of InS - S; b - Photoconductivity of pure S; c - Photoconductivity of layers of InSe - S.

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